Hydrogen Atom:

$$\left\{-\frac{\hbar^2}{2m}\Delta - \frac{e^2}{4\pi\varepsilon_0|\vec{x}|}\right\}\psi(\vec{x}) = E\,\psi(\vec{x})$$

isotropy: spherical coordinates r, ϑ, φ

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\hat{\vec{L}}^2}{\hbar^2 r^2}\right]-\frac{e^2}{4\pi\varepsilon r}\right\}\psi(r,\vartheta,\varphi)=E\,\psi(r,\vartheta,\varphi)$$

$$\hat{\vec{L}}^2 = -\hbar^2\left\{\frac{\partial^2}{\partial\vartheta^2}+\frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right\}$$

separation ansatz: $\psi(r,\vartheta,\varphi) = R(r)\,Y(\vartheta,\varphi)$

spherical harmonics $Y_{lm}(\vartheta,\varphi)$ ← magnetic quantum number

angular momentum quantum number

$$\left.\begin{aligned}\hat{\vec{L}}^2\, Y_{lm}(\vartheta,\varphi) &= \hbar^2 l(l+1)\, Y_{lm}(\vartheta,\varphi)\\ \hat{L}_z\, Y_{lm}(\vartheta,\varphi) &= \hbar m\, Y_{lm}(\vartheta,\varphi)\end{aligned}\right\}\quad \begin{aligned} l &= 0, 1, 2, 3, \ldots\\ m &= -l, -l+1, \ldots, l-1, l\end{aligned}$$

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

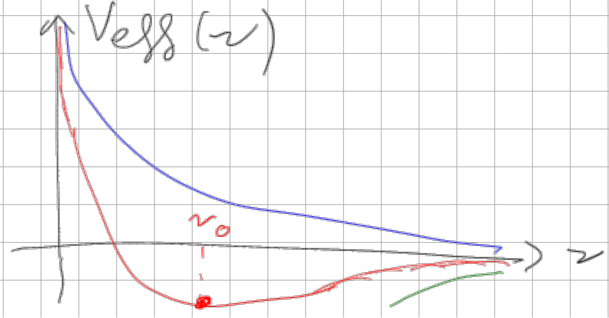
Radial Part:

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\cancel{\frac{2}{r}\frac{d}{dr}}\right)+\frac{\hbar^2 l(l+1)}{2m r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right\}R(r) = E\,R(r)$$

1) $R(r) = \dfrac{u(r)}{r}$, $\displaystyle\int_0^\infty dr\, \underbrace{r^2 R(r)^2}_{u^2(r)} \stackrel{!}{=} 1$ normalization

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\underbrace{\frac{\hbar^2 l(l+1)}{2m r^2}-\frac{e^2}{4\pi\varepsilon_0 r}}_{=V_{eff}(r)}\right\}u(r) = E\,u(r)$$

→ effectively one-dimensional



2) small radii: $r \to 0$

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right] u(r) = 0$$

$u(r) = r^\alpha$, $u'(r) = \alpha r^{\alpha-1}$, $u''(r) = \alpha(\alpha-1) r^{\alpha-2}$

$\alpha(\alpha-1) r^{\alpha-2} - l(l+1) r^{\alpha-2} = 0 \Rightarrow \alpha^2 - \alpha - l(l+1) = 0$

$\Rightarrow \alpha_1 = l+1, \quad \alpha_2 = -l$

$u(r) = \underline{A r^{l+1}} + \cancel{B \frac{1}{r^l}}$ ← discard due to normalizability

3) large radii: $r \to \infty$

$$\left(\frac{d^2}{dr^2} + \frac{2mE}{\hbar^2}\right) u(r) = 0 \quad ; \quad E < 0 \quad \text{bound states}$$

$$\varkappa = \sqrt{-\frac{2mE}{\hbar^2}}$$

$$\left(\frac{d^2}{dr^2} - \varkappa^2\right) u(r) = 0 \Rightarrow u(r) = A e^{-\varkappa r} + \cancel{B e^{+\varkappa r}}$$

4) $u(r) = r^{l+1} e^{-\varkappa r} v(r)$

$$\frac{du}{dr} = \left\{ r \frac{dv}{dr} + (l+1-\varkappa r) v \right\}$$

$$\frac{d^2u}{dr^2} = \text{----}$$

insert in Schrödinger equation, multiply by $\frac{2m}{\hbar^2}$

$$\left\{ r \frac{d^2}{dr^2} + 2(l+1-\varkappa r) \frac{d}{dr} - \left[2\varkappa(l+1) - \frac{e^2 m}{2\pi \varepsilon_0 \hbar^2}\right] \right\} v = 0$$

5.) $\boxed{y = 2\kappa r}$, $\quad v(r) = \phi(2\kappa r)$, $\quad \phi(y) = v\left(\frac{y}{2\kappa}\right)$

$$\left\{ y\frac{d^2}{dy^2} + (2\ell+2-y)\frac{d}{dy} - \left(\ell+1-\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa}\right)\right\}\phi(y)=0$$

$$\left\{ y\frac{d^2}{dy^2} + (c-y)\frac{d}{dy} - a\right\}\phi(y)=0$$

Kummer equation

$$a = \ell+1-\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa}, \qquad c = 2\ell+2$$

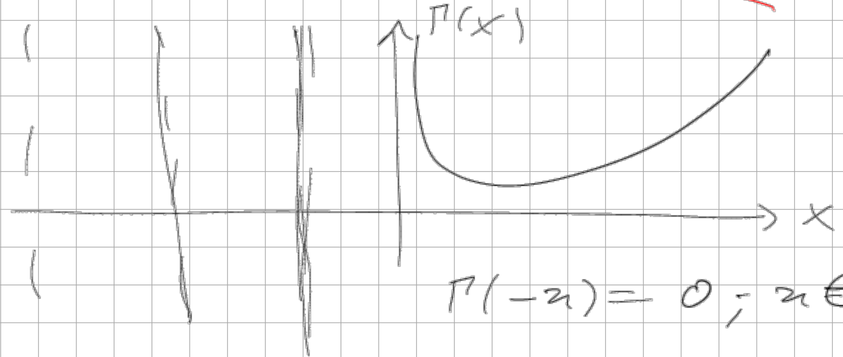
$$\phi(y) = A\,{}_1F_1(a;c;y) + B\,y^{1-c}\,{}_1F_1(a+1-c;2-c;y)$$

due to normalizability

$$\phi(y) = A\,{}_1F_1\left(\ell+1-\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa};2\ell+2;y\right) + \cancel{B\,y^{-2\ell-1}\,{}_1F_1\left(-\ell-\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa};-2\ell;y\right)}$$

$${}_1F_1(a;c;y) = \sum_{r=0}^{\infty}\frac{(a)_r}{(c)_r}\frac{y^r}{r!}$$

$$(c)_r = \frac{\Gamma(c+r)}{\Gamma(c)}$$



$\Gamma(-n) = 0;\ n\in\mathbb{N}$

truncation condition:

$$a = \boxed{\ell+1-\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa}} \overset{!}{=} -n_r; \qquad n_r = 0,1,2,\ldots \text{ radial quantum number}$$

$$\frac{e^2 m}{4\pi\varepsilon_0\hbar^2\kappa} = n_r+\ell+1 =: n; \quad \text{principal quantum number}$$

$$\kappa = \frac{e^2 m}{4\pi\varepsilon_0\hbar^2}\frac{1}{n} = \sqrt{-\frac{2m}{\hbar^2}E} \Rightarrow E_n = -\underbrace{\frac{\hbar^2}{2m}\frac{e^4 m^2}{16\pi^2\varepsilon_0^2\hbar^4}}_{1\,Ry}\frac{1}{n^2}$$

$$\kappa = \sqrt{+\frac{2m}{\hbar^2}\frac{\hbar^2}{2m a_B^2}\frac{1}{n^2}} = \frac{1}{a_B n} \qquad \frac{\hbar^2}{2m a_B^2} = \frac{1}{2}mc^2\alpha^2 = 1\,Ry = \frac{e^4 m}{32\pi^2\varepsilon_0^2\hbar^2}$$

$$\alpha = \frac{e^2}{4\pi \varepsilon_0 \hbar \varepsilon_0 c} = \frac{\lambda_c}{2\pi a_B} = 0.0073 \approx \frac{1}{137}$$

$$\lambda_c = \frac{2\pi \hbar}{mc}, \quad a_B = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2}$$

$$\left| \begin{array}{l} n_r = 0 \Rightarrow \\ n_r = 1 \Rightarrow \\ \vdots \\ n_r = n-1 \Rightarrow \end{array} \right. \boxed{\begin{array}{l} l = n-1 \\ l = n-2 \\ \\ l = 0 \end{array}} \Bigg\} \; l = 0, 1, 2, \ldots, n-1$$

$$R(r) = \frac{u(r)}{r}, \quad u(r) = r^{l+1} e^{-\varkappa r} v(r), \quad v(r) = \phi(\underbrace{2\varkappa r}_{= y})$$

$$R(r) = \frac{1}{r} r^{l+1} e^{-\varkappa r} {}_1F_1(-n_r; 2l+2; \underline{2\varkappa r}) \qquad \begin{array}{l} n = n_r + l + 1 \\ n_r = n - l - 1 \end{array}$$

(18.972.1) Gradshteyn:
$$L_n^{(\alpha)}(x) = \binom{n+\alpha}{n} {}_1F_1(-n; \alpha+1; x)$$

Laguerre polynomial

(18.972.2) $H_{2n}(x) = (-1)^n 2^{2n} n! \, L_n^{(-\frac{1}{2})}(x^2)$

(18.972.3) $H_{2n+1}(x) = (-1)^n 2^{2n+1} n! \, L_n^{(1/2)}(x^2)$

} harmonic oscillator

$$R_{nl}(r) = N r^l L_{n-l-1}^{(2l+1)}\left(\frac{2r}{a_B n}\right) e^{-\frac{r}{a_B n}}$$

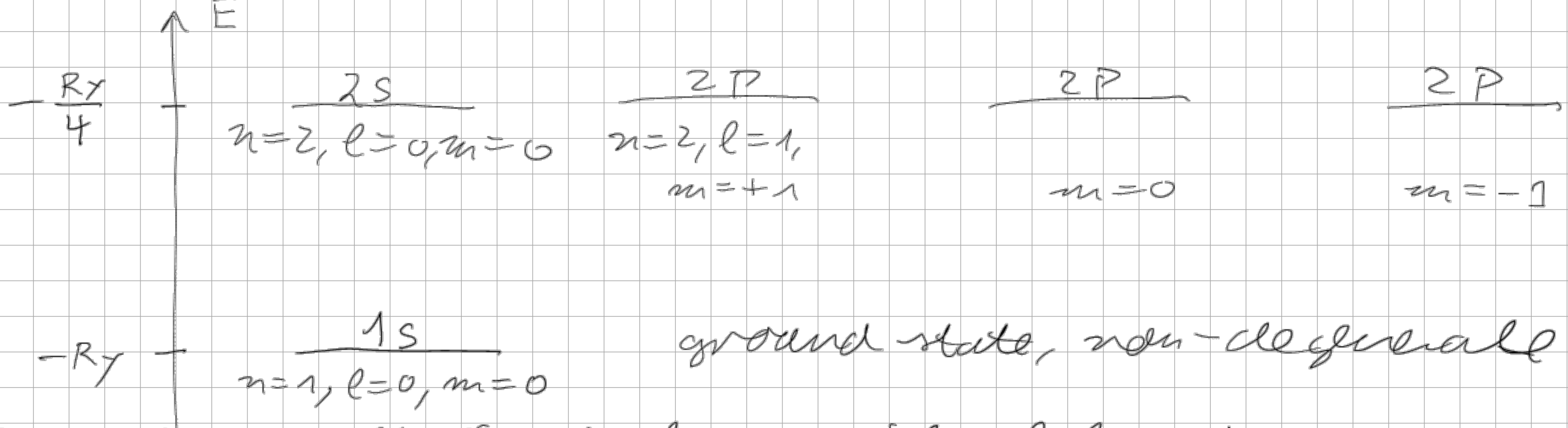
$$= \frac{2}{n^2 a_B^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left(\frac{2r}{a_B n}\right)^l L_{n-l-1}^{(2l+1)}\left(\frac{2r}{a_B n}\right) e^{-\frac{r}{a_B n}}$$

Time-Independent Degenerate Perturbation Theory

Hydrogen Atom:

$$E_n = -R_Y \frac{1}{n^2}; \quad n = 1, 2, \ldots$$

degeneracies with respect to l, m: $d_n = n^2$



first excited states degenerate $d_2 = 4$

ground state, non-degenerate

Concrete application to be considered later:
apply additional spatio-temporal homogeneous electric field

$$\vec{E} = \mathcal{E}\, \vec{e}_z \quad \Rightarrow \text{Stark effect}$$

- first excited states: partial lift of degeneracy $\rightarrow$ linear Stark effect
- ground state: quadratic Stark effect (downward shift)

Starting Point:

$$\hat{H}_0 \, |\psi^{(0)}_{n\,\alpha_n}\rangle = \underbrace{E^{(0)}_n}_{\text{not depend on } \alpha_n \text{ due to assumed degeneracy}} |\psi^{(0)}_{n\,\alpha_n}\rangle$$

$\alpha_n = 1, \ldots, d_n$

$|\psi^{(0)}_{n1}\rangle, \ldots, |\psi^{(0)}_{n\,d_n}\rangle$: d_n degenerate states

$$\langle \Psi^{(0)}_{n n\alpha_n} | \Psi^{(0)}_{m\beta_m} \rangle = \underbrace{\delta_{\alpha_n,\beta_n}}_{\text{Schmidt orthonormalization}} \underbrace{\delta_{n,m}}_{=0,\ n\neq m:\ \text{always true}}$$

$$\underbrace{\hat{H}(\lambda)}_{=\hat{H}_0+\lambda\hat{V}} |\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle = E_{n\underbrace{\alpha_n}_{\text{degeneracy can be lifted due to } \vec{V}}}(\lambda)\, |\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle$$

$$|\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle = \boxed{\underbrace{|\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle}_{\neq |\Psi^{(0)}_{n\alpha_n}\rangle}} + \lambda |\tilde{\Psi}^{(1)}_{n\alpha_n}\rangle + \cdots$$

1. result

$$E_{n\alpha_n}(\lambda) = E^{(0)}_n + \lambda \boxed{E^{(1)}_{n\alpha_n}} + \cdots$$

2. result